# PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

# **MAY 2001 SAMPLING EVENT**



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## Pesticide Monitoring Project Report May 2001 Sampling Event

#### Executive Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 40 sites were collected from May 14 to May 22, 2001, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides ametryn, atrazine, bromacil, diuron, hexazinone, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, beta ( $\beta$ ) endosulfan, endosulfan sulfate, and naled were detected in one or more of these surface water samples.

The herbicide ametryn, together with the insecticides/degradates DDD, DDE, DDT, dieldrin, alpha ( $\alpha$ ) endosulfan, beta ( $\beta$ ) endosulfan, endosulfan sulfate, ethion, and hexazinone were found in the sediment at several locations, along with one PCB compound. Some of the detected sediment concentrations of DDD, DDE, and the PCB compound are usually associated with the potential for impacting wildlife when compared to coastal sediment quality assessment guidelines. The DDT, one of the PCB, and two of the DDD detections were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at the District's sampling sites.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

#### **Background and Methods**

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards applies. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-six pesticides and degradation products were analyzed for in samples from all of the 40 sites, with the exception of the organochlorine compounds at S-332 (Figure 1). Sites S355A and S355B were added to the monitoring network at the request of the United States Army Corps of Engineers to evaluate water quality leaving WCA3B and entering the Everglades National Park. The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994a) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC<sub>50</sub> or LC<sub>50</sub> reported in the summarized literature. Sediment concentrations are compared to coastal sediment quality assessment guidelines (FDEP, 1994b), as there are no corresponding freshwater sediment quality assessment guidelines. A value below the threshold effects level (TEL) should not have an impact on wildlife. The value between the TEL and probable effects level (PEL) has a possibility for impacts, while those exceeding the PEL have a substantial probability for impacting wildlife. This summary covers surface water and sediment samples collected between May 14 to May 22, 2001.

### Findings and Recommendations

At least one pesticide was detected in surface water at 38 of the 40 sites and in sediment at 13 of the 36 sites. Sediment samples are not routinely collected at GORDYRD, CR33.5T, NSIDWC06, and NSIDWC07. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. With the exception of naled, all these compounds have previously been detected in this monitoring program.

Endosulfan ( $\beta$ ) was detected at only one location (S178) in the south Miami-Dade farming area (Table 2). However, this concentration does not exceed the Florida Class III surface water quality standard (Chapter 62-302) (Figure 3). Endosulfan ( $\alpha$  and  $\beta$ ) was quantified in the sediment at the same sampling location (Table 3). However, no sediment quality assessment guidelines have been developed for endosulfan as insufficient data exists (FDEP, 1994b).

Some of the detected sediment concentrations of DDD, DDE, and the PCB compound are usually associated with the potential for impacting wildlife when compared to coastal sediment quality assessment guidelines. The DDT, one of the PCB, and two of the DDD detections were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at the District's sampling sites.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

#### Usage and Water Quality Impacts

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations >  $10 \,\mu\text{g/L}$  (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour  $LC_{50}$  of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.0099 to 0.12  $\mu\text{g/L}$ . Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The sediment concentrations ranged from 8.5 to  $17 \,\mu\text{g/Kg}$ . However, no sediment quality assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC50 of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210  $\mu$ g/L for bluegill and fathead minnow (Verschueren, 1983). The atrazine surface water concentrations found in this sampling event at 36 of the 40 sampling locations, ranged from 0.015 to 2.2  $\mu$ g/L. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Atrazine was not quantified in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio, on a molar basis, (DAR) has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). Most of the sites fall in this category with the exception of S178. The DAR value of 0.9 suggests considerable degradation of atrazine has occurred in this basin. However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop

areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour  $LC_{50}$  of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at S99 (0.65  $\mu$ g/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish. Bromacil was not quantified in the sediment.

<u>DDE</u>, <u>DDD</u>, <u>DDT</u>: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichlorodiphenyltrichloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichlorodiphenyldichloroethane), and the high  $K_{oc}$  of these compounds accounts for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

Sediment quality assessment guidelines have been developed for several metals and organic compounds in coastal sediments (FDEP, 1994b). The DDD concentrations detected range from 2.3 to 27  $\mu$ g/Kg. Those values, which are between the TEL (1.2  $\mu$ g/Kg) and PEL (7.8  $\mu$ g/Kg), have the possibility for impacting wildlife. Two of the values (25  $\mu$ g/Kg at S5A, and 27  $\mu$ g/Kg at S6) exceed the PEL and are considered to represent significant and immediate hazard to aquatic organisms.

The TEL is 2.1  $\mu$ g/Kg and the PEL is 374  $\mu$ g/Kg for DDE in coastal sediments. All of the DDE concentrations detected (5.2 to 42  $\mu$ g/Kg) are between the TEL and PEL. The levels between the TEL and PEL have the possibility for impacting wildlife as they have exceeded the threshold level.

The only DDT concentration detected (13  $\mu$ g/Kg at S5A) exceeds the PEL (4.8  $\mu$ g/Kg). This level is considered to represent a significant and immediate hazard to aquatic organisms.

<u>Dieldrin</u>: Dieldrin is a non-systemic insecticide with all uses canceled in the United States (Hartley and Kidd, 1987). The high  $K_{oc}$  and low water solubility accounts for dieldrin's affinity for sediment. The hydrophobicity of this compound also results in a significant bioconcentration factor and the potential for a high degree of accumulation in aquatic organisms (Table 4). Dieldrin is highly toxic to mammals. Sediment quality assessment guidelines have been developed for dieldrin in coastal sediments (FDEP, 1994b). The level detected in the sediment at S79 (9.5 μg/Kg) is above the PEL (4.3 μg/Kg). This level of dieldrin has a possibility for impacting wildlife. No dieldrin was detected in the surface water.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate

significantly. Additional fish toxicity data includes a 96-hour LC<sub>50</sub> of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48 hour LC<sub>50</sub> of 1.4 mg/L for water fleas and a 96 hour LC<sub>50</sub> of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10  $\mu$ g/L (Verschueren, 1983). The highest concentration of diuron found during this sampling event was 0.89  $\mu$ g/L (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the  $\alpha$  (alpha) and the  $\beta$  (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD50 for rats of 70 mg/Kg (Hartley and Kidd, 1987). The Soil Conservation Service rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4).  $\beta$ -endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. A bioconcentration factor of 1,267 indicates a low to moderate degree of accumulation in aquatic organisms (Lyman et al., 1990). Endosulfan ( $\beta$ ) was detected at only one location (S178) in the south Miami-Dade farming area (Table 2). However, this concentration does not exceed the Florida Class III surface water quality standard (Chapter 62-302) (Figure 3). Endosulfan ( $\alpha$  and  $\beta$ ) was quantified in the sediment at the same sampling location (Table 3). However, no sediment quality assessment guidelines have been developed for endosulfan as insufficient data exists.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The surface water detections occurred at two of the Miami-Dade farming sites as well as ACME1DS. No FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate, nor do these concentrations exceed the Florida Class III surface water standard of  $0.056~\mu g/L$ , for the parent compound, endosulfan. Endosulfan sulfate was detected in the sediment at S178 (42  $\mu g/Kg$ ). However, no sediment quality assessment guidelines have been developed for endosulfan sulfate.

Ethion: Ethion is a non-systemic acaricide and insecticide registered for use on several fruits, citrus, and vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethion (1) is strongly sorbed to soil and therefore can accumulate in sediments; (2) is slightly toxic to mammals, relatively toxic to fish and extremely toxic to Daphnia; and (3) bioconcentrates to a limited extent. Several sources of toxicity information have shown both agreement and disagreement of these laboratory tests. No ethion was detected in the surface water (Figure 2). With the method detection limit around 0.019  $\mu$ g/L, any detection will automatically exceed the calculated chronic toxicity (0.003  $\mu$ g/L) for *Daphnia magna*.

Ethion was detected in the sediment at S99 (4.0  $\mu g/Kg$ ) and S176 (6.6  $\mu g/Kg$ ). However, no sediment quality assessment guidelines have been developed for ethion.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC<sub>50</sub> of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at S140 (1.7 μg/L) should not have an acute impact on fish or aquatic invertebrates. Hexazinone was also detected in the sediment at FECSR78 (69 μg/Kg). However, no sediment quality assessment guidelines have been developed for hexazinone.

Naled: Naled is a non-systemic insecticide and acaricide registered for use on many crops, including fruits and vegetables, as well as rice and ornamentals. Additional use is for the control of mosquitoes. Environmental fate and toxicity data in Tables 4 and 5 indicate that naled (1) is not readily lost from leaching or surface adsorption and only a moderate potential for loss due to surface solution; (2) is moderately toxic to mammals and fish; and (3) does not bioconcentrate significantly. This is the first time naled has been detected in the monitoring network. The only surface water concentration  $(0.23 \,\mu\text{g/L})$  at S5A) should not have an acute detrimental impact on fish or aquatic invertebrates. Naled was not detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC<sub>50</sub> for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.023 to 1.3  $\mu$ g/L. Even at the highest concentration, this is over an order of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 is a commercial grade mixture containing 54% chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. Florida sediment quality assessment guidelines has been developed for total PCBs in coastal sediments (FDEP, 1994b). However, an evaluation of the reliability of the sediment quality assessment guidelines for total PCBs suggests a low degree of confidence can be placed on these guidelines due to the insufficient data used in their development. The TEL is 21.6 μg/Kg and the PEL 189 μg/Kg for PCB's. The sediment residue detected at S79 (78 μg/Kg) has a possibility

for impacting wildlife, while the concentration detected at S7 (237  $\mu g/Kg$ ) represents a significant and immediate hazard to aquatic organisms. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC<sub>50</sub> of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500  $\mu$ g/L (Verschueren, 1983). Aquatic invertebrate LC<sub>50</sub> toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine was detected at S5A (0.50  $\mu$ g/L), below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

### Quality Assurance Evaluation

Five duplicate samples were collected at sites S176, S355B, S7, S2, and S235. All the analytes detected in the surface water had precision ≤30% RPD. No analytes were detected in the field blanks collected at S9, S5A, and S4. No analytes were detected in the three equipment blanks performed at S18C, S38B, and S99. All samples were shipped and all bottles were received, with the exception of the organochlorine compounds at S-332. This sample expired for preparation due to re-extraction.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. Matrix spike recoveries and precision measurements (relative percent difference) for 2,4-T and silvex did not meet the specified requirements for the sediment samples collected at the following locations: S79, S78, S235 including field duplicate) FECSR78, S65E, S191, S99, S80, S2 (including field duplicate), S3, and S4 (including field blank). The matrix spike recoveries for the sediment samples collected at S331, G211, US4125, S12C, S355A, S355B (including field duplicate), and S31 for alachlor, metolachlor, and prometryn did not meet the specified requirements. The lab fortified blank and matrix spike recoveries for atrazine desisopropyl and butylate did not meet the specified requirements for the surface water samples collected at the following locations: S331, G211, US4125, S12C, S355A, S355B (including field duplicate), S31, S9 (including field blank), G123, S142, S140, S190, L3BRS, S8 (including equipment blank), S38B, S7 (including field duplicate), NSIDWC06, NSIDWC07, S6, S5A, (including field blank), ACME1DS, and G94D. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

#### **Glossary**

- LD<sub>50</sub>: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LC<sub>50</sub>: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- EC<sub>50</sub>: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.
- Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

#### Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

#### Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

- MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.
- PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.
- TEL: The threshold effects level represents the upper limit of the range of sediment contaminant concentrations dominated by no effect data entries, or the minimal effects range. Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms
- PEL: The probable effects level was calculated to define the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects or the lower limit of the probable effects range. Within the probable effects range, concentrations of sediment-associated contaminants are considered to represent significant and immediate hazards to aquatic organisms.

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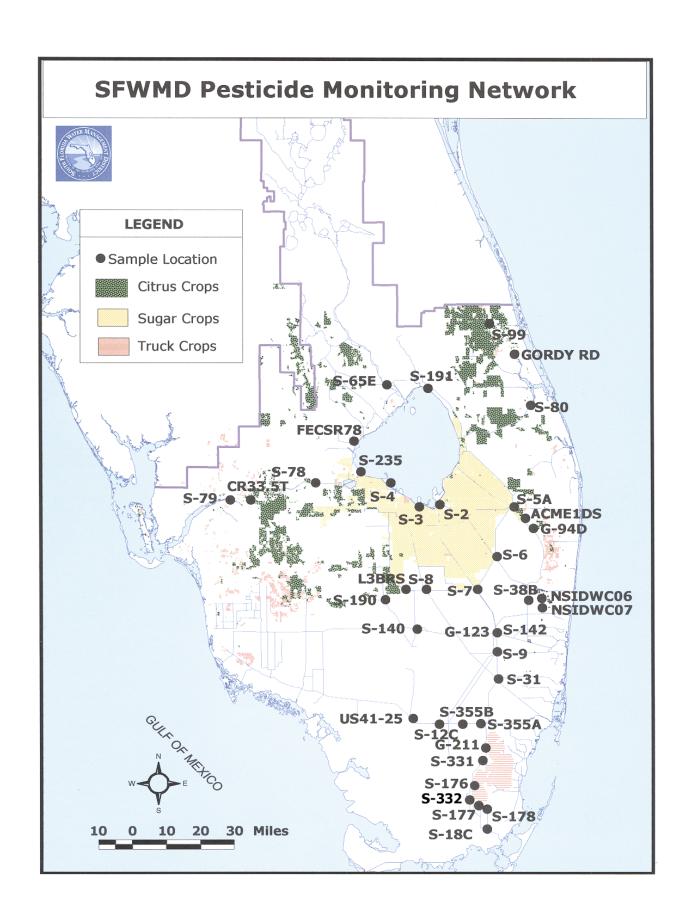


Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in May 2001.

determined in May			Τ=		
Pesticide	Water	Sediment	Pesticide	Water	Sediment
or	range of	range of	or	range of	range of
metabolite	MDL-PQL	MDL-PQL	metabolite	MDL-PQL	MDL-PQL
	(µg/L)	( µg/Kg)		(µg/L)	(µg/Kg)
2,4-D	0.8 - 3.2	17 - 680	endosulfan sulfate	0.0046 - 0.0236	0.98 - 32
2,4,5-T	0.8 - 3.2	17 - 680	endrin	0.019 - 0.1	2 – 64
2,4,5-TP (silvex)	0.8 - 3.2	17 - 680	endrin aldehyde	0.0038 - 0.0216	0.98 - 32
acifluorfen	NA	17 - 680	ethion	0.019 - 0.1	2.1 – 80
alachlor	0.048 - 0.248	29 - 960	ethoprop	0.019 - 0.1	4.3 – 160
aldrin	0.0019 - 0.0108	0.49 - 15.2	fenamiphos (nemacur)	0.029 - 0. 148	17 - 640
ametryn	0.0095 - 0.048	2.1 - 80	fonofos (dyfonate)	0.019 - 0.1	4.3 - 160
atrazine	0.0095 - 0.192	2.1 - 80	heptachlor	0.0023 - 0.012	0.49 - 15.2
atrazine desethyl	0.0095 - 0.048	NA	heptachlor epoxide	0.0019 - 0.01	0.49 - 15.2
atrazine desisopropyl	0.0095 - 0.048	NA	hexazinone	0.019 - 0.1	8.6 - 320
azinphos methyl (guthion)	0.019 - 0.1	2.1 - 80	imidacloprid	0.2 - 0.4	NA
α-BHC (alpha)	0.0021 - 0.0108	0.49 - 15.2	linuron	0.2 - 0.4	8.6 - 160
β-BHC (beta)	0.0019 - 0.0168	0. 49 - 15.2	malathion	0.029 - 0.148	6.4 - 240
δ-BHC (delta)	0.00095 - 0.01	0.98 - 32	metalaxyl	0.048 - 0. 248	NA
γ-BHC (gamma) (lindane)	0.00095 - 0.01	0.49 - 15.2	methamidophos	NA	21 - 800
bromacil	0.038 - 0.196	17 - 640	methoxychlor	0.0099 - 0.052	2.4 - 80
butylate	0.019 - 0.1	NA	metolachlor	0.057 - 0.296	21 - 800
carbophenothion (trithion)	0.015 - 0.08	1.7 - 80	metribuzin	0.019 - 0.1	4.3 -160
chlordane	0.0095 - 0.048	7.3 - 240	mevinphos	0.057 - 0.296	8.6 - 320
chlorothalonil	0.015 - 0.08	2.4 - 80	mirex	0.011 - 0.06	2.0 - 64
chlorpyrifos ethyl	0.019 - 0.1	2.1 - 80	monocrotophos (azodrin)	NA	43 - 1600
chlorpyrifos methyl	0.0095 - 0.048	4.3 - 160	naled	0.076 - 0.398	35 - 1280
cypermethrin	0.019 - 0.1	NA	norflurazon	0.019 - 0.1	4.3 - 160
DDD-p,p'	0.0019 - 0.0216	0.98 - 32	parathion ethyl	0.019 - 0.1	6.4 - 240
DDE-p,p'	0.0038 - 0.0196	0.98 - 32	parathion methyl	0.019 - 0.1	6.4 - 240
DDT-p,p'	0.0038 - 0.0196	1.5 - 48	PCB	0.019 - 0.1	10 - 720
demeton	0.11 - 0.6	43 -1160	permethrin	0.015 - 0.08	NA
diazinon	0.019 - 0.1	4.3 - 160	phorate	0.029 - 0.148	2.1 - 80
dicofol (kelthane)	0.042 - 0.216	7.3 - 240	prometryn	0.019 - 0.1	6.4 - 240
dieldrin	0.0019 - 0.01	0.49 - 15.2	simazine	0.0095 - 0.048	2.1 - 80
disulfoton	0.019 - 0.1	4.3 - 160	toxaphene	0.071 - 0.368	37 - 1200
diuron	0.2 - 0.4	8.6 - 160	trifluralin	0.0076 - 0.0396	2.0 - 64
α-endosulfan (alpha)	0.0038 - 0.0196	0.49 - 15.2			
β-endosulfan (beta)	0.0038 - 0.0196	0.49 - 15.2			
· · · · ·	•		•	•	

NA – not analyzed

Table 2. Summary of pesticide residues above the method detection limit found in surface water samples collected by SFWMD in May 2001

ы	ω.	Ν						СОМ	POUNDS (μg/L)						Number of
DATE	SITE	FLOW	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diuron	beta endosulfan	endosulfan sulfate	hexazinone	naled	norflurazon	simazine	compounds detected at site
05/14/01	S18C	N	-	0.018 I	-	-	-	-	-			-	-	-	1
00, 01, 01	S178	N	1	0.044	0.033 I	0.016 I	-	-	0.0051 I	0.036	-	-	-	-	5
	S177	N	-	0.039	-	-	-	-	-	0.011 I	-	-	-	-	2
	S332	N	-	-	-	-	-	-	-	-	-	-	-		0
	S176	N	-	0.069 *	-	-	-	-	-	-	-	-	-	-	1
05/15/01	S331	N	-	0.050	-	-	-	-	-	-	-	-	-		1
, , ,	G211	N	-	0.023 I	-	-	-	-	-	-	-	-	-		1
	US41-25	N	1	-	-	-	-	-	-	1	-	-	-	-	0
	S12C	N	-	0.048	-	-	-	-	-	1	-	-	-	-	1
	S355A	N	-	0.018 I	-	-	-	-	-	-	-	-	-	-	1
	S355B	N	-	0.015 *I	-	-	_	-	-	-	-	-	-	-	1
	S31	N	-	0.17	0.017 I	-	-	-	-	-	-	-	-	-	2
05/16/01	S9	N	-	0.17	0.016 I	0.012 I	-	-	-	-	-	-	-	-	3
00/10/01	G123	Y	-	0.14	0.010 I	-	-	0.86	-	-	0.020 I	-	-	-	4
	S142	R	-	0.16	0.016 I	-	-	0.89	-	-	0.021 I	-	-	-	4
	S140	N	-	0.17	0.022 I	-	-	-	-	-	1.7	-	-	-	3
	S190	N	-	0.11	0.013 I	-	-	_	-	-	-	-	0.051 I	-	3
	L3BRS	N	0.037 I	0.66	0.072	0.017 I	-	0.21 I	-	-	-	-	0.036 I	-	6
	S8	N	0.12	2.0	0.37	-	-	-	-	-	-	-	-	0.013 I	4
05/17/01	S38B	N	0.016 I	1.3	0.14	0.027 I	-	-	-	-	-	-	-	-	4
00/11/01	NSIDWC06	N	0.014 I	1.0	0.13	0.024 I	_	-	-	-	-	_	_	-	4
	NSIDWC07	N	0.018 I	2.2	0.27	0.037 I	-	-	-	-	-	-	-	-	4
	S7	N	0.069 *	1.9 *	0.23 *	-	-	-	-	-	-	-	-	0.043 *	4
	S6	N	0.046	1.2	0.12	0.026 I	_	-	-	-	-	-	-	0.030 I	5
	S5A	N	0.014 I	0.34	0.058	0.024 I	-	-	-	-	-	0.23 I	-	0.019 I	6
	ACME1DS	N	0.041	0.19	0.026 I	_	_	-	_	0.0099 I	_	_	_	_	4
	G94D	N	-	0.14	0.024 I	-	_	-	-	-	-	_	_	-	2
05/21/01	C25S99	N	-	-	-	0.027 I	0.65	-	-	-	-	_	1.3	0.17	4
03/21/01	GORDYRD	N	-	_	_	_	0.22	0.71	_	_	_	_	1.2	0.50	4
	S80	N	-	0.065	0.015 I	-	0.11 I	-	-	-	-	_	0.19	-	4
	S2	N	0.0099 *I	0.36 *	0.061 *	0.017 *I	_	-	-	-	-	_	_	0.019 *I	5
	S3	N	0.013 I	0.27	0.056	0.014 I	-	-	-	-	-	-	-	0.012 I	5
	S4	N	0.016 I	0.29	0.058	0.015 I	-	-	-	-	-	-	-	0.015 I	5
05/22/01	S79	N	0.023 I	0.28	-	-	0.53	0.24 I	-	-	-	_	0.25	0.35	6
50,22,01	CR33.5T	Y	0.018 I	0.41	0.054	0.026 I	0.28	-	-	-	-	-	0.18	0.26	7
	S78	N	0.016 I	0.38	0.082	0.024 I	-	-	-	-	0.37	-	-	0.017 I	6
	S235	N	0.046 *	0.035 *I	-	-	-	-	-	-	0.022 *I	-	-	-	3
	FECSR78	N	-	0.16	0.033 I	0.016 I	0.13 I	-	-	-	-	-	-	0.021 I	5
	S65E	N	-	0.032 I	-	-	0.11 I	-	-	-	-	-	-	0.019 I	3
	S191	N	-	0.039 I	-	-	0.061 I	-	-	-	-	-	0.023 I	-	3
	number of	ı	16	36	24	15	8	5	1	3	5	1	8	14	
compou	ınd detections	3		1	1		1 1	1 ) (D)	İ			0.1.1:	<u> </u>		

N-no Y-yes R-reverse; - denotes that the result is below the MDL; \*-results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Summary of pesticide residues above the method detection limit found in sediment samples collected by SFWMD in May 2001

DATE	SITE						COMPO	UNDS (µg/Kg)	)				Number of	
DATE	SHE	ametryn	DDD	DDE	DDT	dieldrin	alpha endosulfan	beta endosulfan	endosulfan sulfate	ethion	hexazinone	PCB1254	compounds detected at site	
5/14/01	S178	-	-	42	-	-	2.0 I	2.4 I	42	-	-	-	4	
	S177	-	-	5.2	-	-	-	-	-	-	-	-	1	
	S176	-	-	-	-	-	-	-	-	6.6 *I	-	-	1	
5/15/01	S31	-	-	15 I	-	-	-	-	-	-	-	-	1	
	G211	-	-	8.4	-	-	-	-	-	-	-	-	1	
5/17/01	S7	8.5 *I	5.8 *I	-	-	-	-	-	-	-	-	237 *	3	
	S5A	12 I	25	-	13 I	-	-	-	-	-	-	-	3	
	S6	15 I	27	-	-	-	-	-	-	-	-	-	2	
	G94D	-	2.3 I	8.7 I	-	-	-	-	-	-	-	-	2	
5/21/01	CR25S99	-	-	-	-	-	-	-	-	4.0 I	-	-	1	
	S4	17 I	-	-	-	3.6 I	-	-	-	-	-	-	2	
5/22/01	S79	-	-	-	-	9.5	-	-	-	-	-	78 I	2	
	FECSR78	-	-	-	-	-	-	-	-	-	69 I	-	1	
Total number of compound detections		4	4	5	1	2	1	1	1	2	1	2		

<sup>-</sup> denotes that the result is below the MDL; \* - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 4. Selected properties of pesticides found in the May 2001 sampling event.

	FDEP	Florida	$LD_{50}$								
	Surface	Ground	acute								
	Water	Water	rats		Water		soil				
	Standards	Guidance	oral	EPA	Solubility	Koc	half-life				
	62-302	Conc.	(mg/Kg)	Carcinogenic	(mg/L)	(ml/g)	(days)	SCS	rating	(2)	Bioconcentration
Common name	(µg/L)	(μg/L)	(1)	Potential	(2, 3)	(2, 3)	(2, 3)	LE	SA	SS	Factor (BCF)
ametryn	-	63	1,110	D	185	300	60	M	M	M	33
atrazine	-	3**	3,080	C	33	100	60	L	M	L	86
bromacil	-	90	5,200	C	700	32	60	L	M	M	15
DDD-P,P'	-	0.1	3,400	-	0.055	239,900	-	-	-	-	3,173
DDE-P,P'	-	0.1	880	-	0.065	243,220	-	-	-	-	2,887
DDT-P,P'	0.001	0.1	113	-	0.00335	140,000	-	-	-	-	15,377
dieldrin	0.0019	0.1	37 - 87	B2	0.14	10000est.	-	-	-	-	1873
diuron	-	14	3400	D	42	480	90	M	M	L	75
endosulfan, alpha	0.056	0.35	70	-	0.53	12400	50	XS	L	M	884
endosulfan, beta	-	0.35	70	-	0.28	-	-	-	-	-	1267
endosulfan sulfate	-	0.3	-	-	0.117	-	-	-	-	-	2073
ethion	-	3.5	208	-	1.1	8900	150	$\mathbf{S}$	L	M	586
hexazinone	-	231	1,690	D	33,000	54	90	L	M	M	2
naled	-	14	430	-	10	180	1	S	S	M	169
norflurazon	-	280	9,400	C	28	700	90	M	M	L	94
PCB1254	0.014	0.5**	-	B2	-	-	-	-	-	-	-
simazine	-	4**	>5,000	C	6.2	130	60	L	M	M	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large (L), medium (M), small (S) or extra small (XS) Bioconcentration Factor (BCF) calculated as BCF =  $10^{\circ}(2.791 - 0.564 \log WS)$  (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards (12/96) for Class III water except Class I in ()

<sup>\*\*</sup>primary standard

<sup>(1)</sup> Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.

<sup>(2)</sup> Goss, D. and R. Wauchope. (Eds.) (1992). The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure. Soil Conservation Service. Fort Worth, TX.

<sup>(3)</sup> Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.

<sup>(4)</sup> Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington, DC.

<sup>(5)</sup> U.S. Environmental Protection Agency (1996). Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B-96-002.

Table 5. Toxicity of pesticides found in the May 2001 sampling event to selected freshwater aquatic invertebrates and fishes (ug/L).

Common name	48 hr E Water f Daphr Magn	lea nia	acute	chronic toxicity (*)	96 hr LO Fathead Min (#) Pimepha Promela	nnow les	acute toxicity	chronic toxicity	96 hr L0 Bluegi Lepom macroch	ll is	acute toxicity	chronic toxicity	96 hr LC Largemou Bass Micropter salmoide	ith us	acute toxicity	chronic toxicity	96 hr LC Rainbow T (#) Oncorhynd mykiss	rout chus		chronic toxicity	96 hr L0 Chann Catfis Ictaluri punctat	eľ h us	acute toxicity	chronic toxicity
ametryn	28,000	(6)	9,333	1,400	-		-	-	4,100	(4)	1,367	205	-		-	-	8,800	(4)	2,933	440	-		-	-
atrazine	6,900	(6)	2,300	345	15,000	(6)	5,000	750	16,000	(4)	5,333	800	-		-	-	8,800	(4)	2,933	440	7,600	(4)	2,533	380
bromacil	-		-	-	-		-	-	127,000	(6)	42,333	6,350	-		-	-	36,000	(6)	12,000	1,800	-		-	-
DDD-P,P'	3,200	(7)	1,067	160	4,400	(1)	1,467	220	42	(1)	14	2.1	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE-P,P'	-		-	-	-		-	-	240	(1)	80	12	-		-	-	32	(1)	10.7	1.6	-		-	-
DDT-P,P'	-		-	-	19	(5)	6.3	0.95	8	(5)	2.7	0.4	2	(5)	0.7	0.1	7	(5)	2.3	0.35	16	(5)	5.3	0.8
dieldrin	-		-	-	16	(5)	5.3	0.80	8	(4)	2.7	0.4	-		-	-	10	(5)	3.3	0.5	4.5	(5)	1.5	0.23
diuron	1,400	(6	467	70	14,200	(6	4,733	710	5,900	(4)	1,967	295	-		-	-	5,600	(4)	1,867	280	-		-	-
endosulfan	166	(6)	55	8	1	(1)	0.33	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
				-	-		-		2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(6)	0.5	0.08
				-	-		-	-					-			-	1	(3)	0.33	0.050			-	
				-	-		-	-					-			-	0.3	(5)	0.10	0.015			-	
ethion	0.06	(1)	0.02	0.003	720	(1)	240	36	210	(1)	70	11	173	(1)	58	9	500	(1)	167	25	7,600	(1)	2,533	380
				-	-		-	-	13	(3)	4.3	0.65	150	(8)	50	8	193	(3)	64	10	7,500	(8)	2,500	375
				-	-		-	-	22	(8)	7.3	1.1	-			-	560	(8)	187	28			-	-
hexazinone	151,600	(6)	50,533	7,580	274,000	(4)	91,333	13,700	100,000	(6)	33,333	5,000	-		-	-	180,000	(6)	60,000	9,000	-		-	-
naled	-		-	-	3,300	(1)	1,100	165	2,200	(1)	733	110	1,900	(1)	633	95	195	(1)	65	10	710	(1)	237	36
norflurazon	15,000	(6)	5,000	750	-		-	-	16,300	(6)	5,433	815	-		-	-	8,100	(6)	2,700	405	>200,000	(4)	>67,000	>10,000
simazine	1,100	(6)	367	55	100,000	(6)	33,333	5,000	90,000	(4)	30,000	4,500	-		-	-	100,000	(6)	33,333	5,000	-		-	-

<sup>(\*)</sup> Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC<sub>50</sub> is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

<sup>(1)</sup> Johnson, W. W. and M.T. Finley (1980). Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

<sup>(2)</sup> U.S. Environmental Protection Agency (1977). Silvacultural Chemicals and Protection of Water Quality. Seattle, WA. EPA-910/9-77-036.

<sup>(3)</sup> Schneider, B.A. (Ed.) (1979). Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003

<sup>(4)</sup> Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.

<sup>(5)</sup> Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.

<sup>(6)</sup> U.S. Environmental Protection Agency (1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, D.C.

<sup>(7)</sup> Verschueren, K. (1983). Handbook of Environmental Data on Organic Chemicals. Second Edition, Van Nostrand Reinhold Co. Inc., New York N.Y.

<sup>(8)</sup> U.S. Environmental Protection Agency (1972). Effects of Pesticides in Water: A Report to the States. U.S. Government Printing Office. Washington, D.C.

<sup>(9)</sup> Mayer, F.L., and M.R. Ellersieck. (1986). Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals. U.S. Fish and Wildlife Service, Publication No. 160

Figure 2. Ethion Concentration in Surface Water at S99

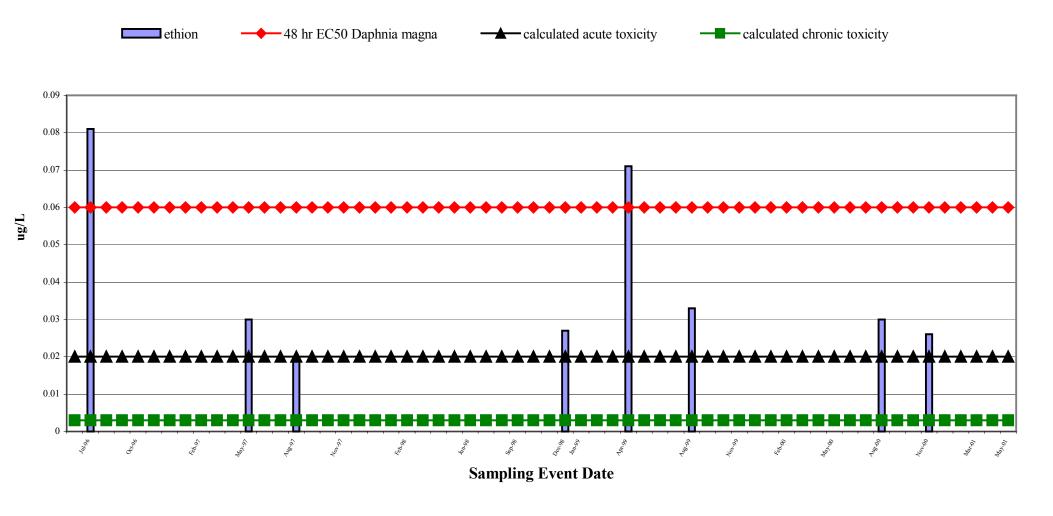


Figure 3. Endosulfan Concentration in Surface Water at S178

